An in-depth look at Corrosive Sulphur and its effect on Transformers

Removing corrosive deposits from metal surfaces and paper is extremely difficult, if possible, at all. The only remedy would be to take the unit out of service.

Removing corrosive deposits from metal surfaces and paper is extremely difficult, if possible, at all. The only remedy would be to take the unit out of service.

Copper sulfide has been identified as the most corrosive compound that might be formed during chemical reactions in the transformer when reactive sulfur compounds are present. Metal sulfides can cause overheating because they may form a resistive layer on various surfaces in the transformer. On bushings, the copper sulfide on a conductor can indicate the ongoing corrosion process but might not be the cause of failure.

Corné Dames is the Managing Director of Independent Transformer Consultants, always striving to keep on top of new developments and research. She has expertise as Laboratory Manager in the analysis of transformer oils and as diagnostician identifying problem areas in transformers, as well as profiling of transformers according to available results thus empowering the customer to take preventative steps in maintenance. Corné has vast practical and theoretical knowledge on reliability maintenance programs. Coming from a strong chemical background she has insight in all the chemical processes that are part of the transformer system. Coupled with technical insight, her knowledge and experience help customers optimize their reliability maintenance and electrical asset lifetime.

Introduction

Many transformer and equipment failures have been reported due to the effect of corrosive sulfur in oil-filled equipment. It is vitally important to look at condition monitoring and maintenance approaches in this type of scenario. The first question that comes to mind is, how is it possible for oil with corrosive sulfur compounds to have slipped through the quality control net of transformer oil diagnostics? Is it possible that the standardized tests cannot accurately identify oils with this corrosive compound? This has been the case before the IEC 60422 recommended ASTM 1275B and IEC 62353 as the applicable methods for determining corrosive sulfur. These methods will ensure greater accuracy in determining corrosive sulfur compounds in transformer oil.

It should be noted that oils with a high sulfur content do not indicate a highly corrosive compound. The type of sulfur molecule needs to be identified to establish the severity of the reactive nature of the sulfur variant in the oil.

Units containing varnished or enamel-coated wires or thermally upgraded kraft paper are more resistant to the corrosive effect of reactive sulfur.

It was found that this corrosive reaction is time and *temperature-dependent*. Higher temperatures can lead to greater corrosion and larger amounts of metal sulfide formation. Sealed units are more susceptible to this problem; in free-breathing units, the oxygen and corrosive sulfur compounds compete for reaction sites on the copper and organometallic compounds. This slows down the formation of the conductive metal sulfides in free-breathing units but does not stop it.

We will discuss:

- Effect of corrosive sulfur
- The different forms of sulfur that might be present in transformer oils.
- The sources of sulfur in transformer oils
- Acceptable values for Corrosive Sulfur in new and reclaimed oils
- Test methods for Corrosive Sulfur detection
- The chemistry behind the formation of corrosive sulfur in transformer systems
- Electrical testing
- Condition monitoring of units with possible and definite contamination with corrosive sulfur
- Maintenance approaches for oils with corrosive sulfur.

Corrosive sulfur effects

Corrosive sulfur leads to the formation of insoluble substances in oil, precipitate as sludge, or form copper sulfide deposits on copper conductors and paper insulating tapes. [1] During the inspection of transformers and shunt reactors windings, it was noted that the copper sulfide migrates within the paper layers of the insulating paper. In most cases, the copper sulfide concentration tends to be highest within the inner tape layers adjacent to the copper conductors; the tendency is to diffuse outwards.

A plausible explanation for this observation is that the higher concentration gradient of copper is at the surface of the copper conductor. It should also be noted that there is an increased temperature gradient effect at the copper conductor surface or in its vicinity due to the high currents carried by the copper conductor. This will add to the increase of the reaction rate for the formation of copper sulfide due to the presence of corrosive sulfur and copper and high temperatures.

The different types of sulfur that might be present in transformer oils

The accepted scale of corrosiveness places elemental sulfur as the most corrosive element against copper, followed by hydrogen sulfide, mercaptans, sulfides, and disulfides. In compounds where the sulfur atom is part of an aromatic structure, the compound is considered non-reactive.

Sulfur is a common component found in crude oil as this substance is found in 0.5% of the earth's crust. Organic sulfur compounds are more reactive than inorganic types. Some sulfur compounds can aid in the oxidation stability of transformer oil. It might act as a metal passivator and deactivator by reducing the catalytic effect on oil oxidation. The manufacturer aims to remove or convert the reactive-corrosive sulfur compounds to more stable compounds like thiophenes and saturated disulfides during the refining process.

The steps implemented during the refining process to achieve the removal or conversion of reactive sulfur compounds are:

a) Atmospheric distillation at various temperatures.
b) Vacuum distillation
c) Catalytic reaction
d) Hydro-treating
e) Hydro-generation

It should be noted that there might be some incomplete refining that would leave small amounts of mercaptans, or the hydrogenation process may produce elemental sulfur instead of hydrogen sulfide.

How does corrosive and reactive sulfur react in the transformer environment?

When corrosive and reactive sulfur comes into contact with copper and other metals, it can react. Copper is the most *vulnerable* metal to sulfur attack. The reaction of sulfur to combine with copper is problematic as it does not need high temperatures. It should be noted that different grades of copper contain different levels of oxygen. The design engineer needs to ensure the correct grade of copper is used for the application. The oxygen in the copper will then react with the reactive sulfur. Reactive sulfur will also react with other metals; the result will be the formation of copper sulfate ($CuSO_4$) or cuprous sulfite ($CuSO_3$), aluminum sulfate [$Al_2(SO4)_3$] and other inorganic sulfates. [3]

From Non-corrosive to corrosive

Through investigation, it has been found that non-corrosive sulfur can become corrosive after being exposed to elevated temperatures on hot metal surfaces and then produce metal sulfides. It might be that the corrosion material can detach from the surface and become discharge nuclei or gas inception nuclei. This is only a concern with oils containing large concentrations of sulfur, not for oils with lower than recommended sulfur concentrations.

Sulfur sources in transformer systems

Sulfur can come from various components in the transformer system; oil is not the only source. Sulfur may also be present in gaskets, water-based glues, copper, and paper insulation contaminated during the paper manufacturing process. There is also the accidental introduction through incompatible hoses used during maintenance processes.

GROUP	CHEMICAL FORMULA	REACTIVITY
Elemental (Free) Sulfur	S	Very Reactive
Mercaptans (Thiols)	R-SH	Very Reactive
Sulfides (Thio-ethers)	R-S-R_1	Reactive
Disulfides	R-S•S-R	Stable
Thiophenes	Five membered ring containing sulfur	Very Stable
R = paraffin with straight or branched chain hydrocarbon or cyclic hydrocarbon		

Table 1: Sulfur and Sulfur compounds found in Crude oil [2]

During the manufacture of nitrile gaskets, sulfur is used as part of the curing process when the hardening of the material is done. All sulfur is supposed to be eliminated from the product by the end of the manufacturing process. When the manufacturing process is incomplete or some steps are skipped, it might be that not all the sulfur is removed. There does not appear to be any standard on what percentage of sulfur should remain in the final product. In some cases, the sulfur content of the end product is not monitored. Some third-party laboratories tests indicate a high concentration of reactive sulfur in some of these products.

Water-based glues used during the manufacturing process to secure the paper insulation may contain sulfur compounds. The amount of sulfur in electrical grade copper is 15ppm or less.

Photo: Shutterstock

The sulfite process used during the pulping process for electrical kraft paper is acidic and uses sulfur dioxide, sulfuric acid, and calcium bisulfite. This is not the primary process used in the manufacture of kraft paper. The primary process used today for producing electrical grade kraft paper is sulfate also called alkaline pulping. Sodium hydroxide and sodium sulfide are used in the "cooking process."

The kraft process is slightly different in that the pulp is intentionally undercooked. This results in a darker substance with exceptional mechanical strength, using the same chemicals like sulfate and alkaline pulping. The pulp fibers in the kraft process do absorb some of the sulfur compounds that cannot be removed via washing/rinsing processes. [3] Doble Materials Laboratory performed analysis to determine how much total sulfur compounds remains in the finished paper products. [2]

It was found that the sulfur content was quite significant in most of the samples.

Accidental contamination of oil with corrosive sulfur and reactive sulfur compounds can be because incompatible hoses have been used, or it might be that the hoses were contaminated by processing equipment used to process sulfur contaminated oil. It has been found that hoses made from natural rubber or gasoline hoses

contain high amounts of sulfur that can be easily transferred to the oil. Care should be taken in selecting hoses to perform any maintenance processes within the transformer as the wrong type of hose can have adverse long-term effects on the transformer unit.

Long term mitigation of copper sulfide

Once the industry became aware of the risks involved due to corrosive sulfur contamination, the question was asked: How can we mitigate the risk on our assets? It comes down to this; every transformer owner needs to evaluate their level of risk and adopt the appropriate strategy to manage it.

Techniques

Statistical evaluation of the survey indicates that metal passivators are most frequently applied, in 88% of the cases, including 5% of re-passivation. Oil change was carried out in 5% of the cases. Oil treatment processes (reclaiming) in removing corrosive sulfur compounds from the oil were performed in 4% of the cases, and the remaining 5% were other techniques or mixed actions. [4]

During the above survey, it was found that corrosive sulfur does not affect all countries worldwide.

PAPER	TOTAL SULFUR CONTENT*	TOTAL SULFATE CONTENT*
Kraft Paper - 1	700 ppm	205 ppm
Kraft Paper - 2	300 ppm	<7.5 ppm
TU-Kraft	700 ppm	158 ppm
Kraft Crepe Paper - 1	600 ppm	93 ppm
Kraft Crepe Paper - 2	500 ppm	30 ppm

* Total sulfur analysis was performed by ASTM Method D 129 and Total Sulfate analysis was performed by EPA Method 300.0

Table 2: Sulfur composition in various electrical papers [2]

Metal passivators

Triazole derivates are used as metal passivators. This substance will chemically adhere to non-enameled, bare copper surfaces, forming a monomolecular layer (a coating on the surface, around 2 mm thick) that blocks copper involvement as a reactant in the copper sulfide formation and hinders copper catalytic activity as an oxidation catalyst. [5],[6],[7],[8].

Metal passivators are polar compounds that tend to be absorbed in the paper and attach to other metal surfaces. The amount of metal passivator spent for coating other metal surfaces has not been quantified but is likely to be very small and below the standard deviation limits for the test method for metal passivator determination. Therefore, it is assumed that negligible amounts of added metal passivator spent for coating of other metal surfaces, whereas a higher amount is spent for absorption in cellulose materials, and this is likely to be more pronounced at elevated temperatures, which speed up transport of metal passivator into the paper [9],[10]

Metal passivators are sometimes called oil passivators, and this is incorrect. Naturally, the oil is the medium of transfer for the metal passivator to the metal surfaces and into the transformer's solid insulation. It should be referred to as "oil containing metal passivator."

The suggested concentration for the metal passivator is 100mg/kg, but amounts up to 200mg/kg in oil may be added to achieve a higher saturation level of the metal passivator layer on the copper surface. Concentrations of less than 50mg/kg of metal passivator are considered ineffective. [11]

Metal passivators and oil condition

The long-term efficiency of metal passivators regarding temperature, oxygen, and oil aging products was investigated. Low base oil quality and higher amounts of acids in aged oils will decrease metal passivator stability.

Photo: Shutterstock

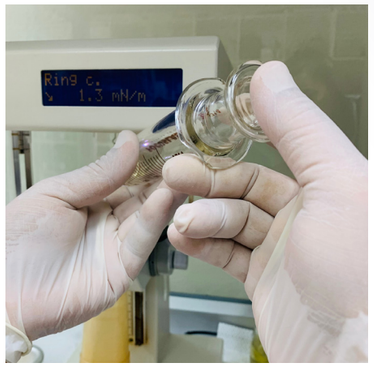
Metal passivators were found to be highly efficient in new oils. The more oxidized the oils were, the metal passivator efficiency decreased. This could be attributed to the degradation of metal passivator under the attack of peroxides and acids.

Conclusion

It is clear from all this that sulfur and sulfur-bearing compounds in transformer mineral oil can present a multi-faceted problem. Refining crude oil aims to remove as many sulfur compounds through various processes, converting reactive compounds into stable ones.

There are many internal and external sources of sulfur within a transformer besides the oil.

Although the corrosive and reactive sulfur reactions can occur at ambient temperatures, it is theorized that higher temperatures may lead to the formation of corrosive or reactive forms of sulfur or reactive forms that allow reactions to occur between some sulfur compounds and metals.



Bibliography

[1] Maina, R. Tumiattia, V. Polpili, M. and Bartnikas, R. *"Corrosive sulfur effects in transformer oils and remedial procedures."*

[2] Lewand, L.R. *"The role of corrosive sulfur in transformers and transformer oil."* Doble Engineering Company, USA, 2002

[3] Casey, James P. Pulp and Paper; Chemistry and Chemical Technology, Interscience Publishers, Inc, New York, 1952.

[4] *"Copper Sulphide Long Term Mitigation and Riks Assessment."* Technical Brochure group A2.40 625, CIGRE, 2015.

[5] Scattigio, F., Pompili, M., Bratnikas, R. Oils with Presence of Corrosive Sulfur: Mitigation and Collateral Effects. Proceedings of *IEEE Electrical Insulation Conference*, Montreal, 2009;478-481

[6] Amimoto, T., Nagao, E., Tanimura, J., Toyama, S., Yamada, N., Duration and Mechanism of Suppressive Effect of Triazole-based Passivators on Copper Sulfide Deposition on Insulating Paper, *IEEE Trans. Dielectr. Electr. Insul. 2009*, 16, 257

[7] Wiklund, P., Levin, M., Pahlavanpour, B., Copper Dissolution and Metal Passivators in Insulating Oil, *IEEE Electrical Insulating Magazine* 2007, 23(4), 1.

[8] Facciotti, M., Amaro, P.S., Brown, R.C.D., Lewin, P., Pilgrim, J.A., Wilson, G., and Jarman, P.N., Passivators, corrosive sulfur and surface chemistry. New tools in the investigation of effective protection. *"My Transfo Proceedings"*, November 2014

[9] *CIGRE TB 378:* Copper sulfide in transformer insulation, 2009

[10] Jelena, M., Lukic, Srdjan Milosavljevic, and Aleksandar M., Orlovic, Degradation of the Insulating System of Power Transformers by Copper Sulfide Deposition: Influence of Oil Oxidation and Presence of Metal Passivator, *Ind. Chem. Res.* 2010, 49, 9600-9608

[11] *IEC 60422:* Mineral Insulating Oils in electrical equipment – Supervision and maintenance guidance, Edition 4.,01-2013